INTERNATIONAL STANDARD

ISO 15651

First edition
2015-02-15

Nuclear energy — Determination of total hydrogen content in PuO_2 and UO_2 powders and UO_2, $(U,Gd)O_2$ and $(U,Pu)O_2$ sintered pellets — Inert gas extraction and conductivity detection method

Énergie nucléaire — Dosage de la teneur totale en hydrogène de poudres de PuO_2 et UO_2, et de pastilles frittées d'UO_2, $(U,Gd)O_2$ et $(U,Pu)O_2$ — Méthode d'extraction par gaz inerte et méthode de mesure de la conductivité

Reference number
ISO 15651:2015(E)

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Published in Switzerland

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword — Supplementary information.

The committee responsible for this document is ISO/TC 85, *Nuclear Energy*, Subcommittee SC 5, *Fuel Technology*.

Nuclear energy — Determination of total hydrogen content in PuO_2 and UO_2 powders and UO_2, $(U,Gd)O_2$ and $(U,Pu)O_2$ sintered pellets — Inert gas extraction and conductivity detection method

1 Scope

This International Standard describes a procedure for measuring the total hydrogen content of UO_2 and PuO_2 powders (up to 2 000 µg/g oxide) and of UO_2 and $(U,Gd)O_2$ and $(U,Pu)O_2$ pellets (up to 10 µg/g oxide). The total hydrogen content results from adsorbed water, water of crystallization, hydrocarbon, and other hydrogenated compounds which can exist as impurities in the fuel.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995)*

3 Principle

The total hydrogen content is determined using a hydrogen analyser. The hydrogen analyser is based on the carrier gas method using argon or nitrogen as carrier gas. The samples to be analysed are heated up to a temperature of more than 1 770 °C in a graphite crucible. At that temperature, all volatile components are removed. The hydrogen containing compounds are cracked and released as hydrogen, oxygen, nitrogen, and carbon monoxide. The released gas is purified in the carrier gas stream, for example by oxidation and adsorption columns. The hydrogen is separated by chromatographic means and analysed in a thermal conductivity cell.

4 Interference

The temperature of >1 770 °C should be reached in a short time, within approximately 5 s; if not, the decomposition of the released water to hydrogen and oxygen might not be complete.

At temperatures of more than 2 200 °C, carbon dioxide is released because of a reduction of UO_2 by graphite according to the reaction below; carbon dioxide will interfere with the thermal conductivity measurement.

$$UO_2 + C \rightarrow UO_{2-x} + x/2\ CO_2$$

5 Reagents and materials

Use reagents of recognized analytical grade. The reagents and materials below serve as examples to be used according to manufacturer recommendation.

5.1 Carrier gas. Use argon with a purity of a volume fraction ≥99,995 % or nitrogen with a purity of a volume fraction ≥99,998 %.

5.2 Calibration gas. If calibration is performed with gas, use Argon or nitrogen with certified hydrogen content or carrier gas mixed with a known amount of hydrogen with a purity of a volume fraction ≥99,999 %.

5.3 Reference material.[1)] If calibration or calibration check is performed with a standard material, use a reference material with certified hydrogen content (e.g. titanium or zirconium).

5.4 Copper(II) oxide, CuO purifies the carrier gas (Ar/N_2), converting H_2 to H_2O.

5.5 Absorption media for H_2O. After converting H_2 to H_2O (§5.4), anhydrone [$Mg(ClO_4)_2$] is used to trap H_2O.

5.6 Oxidation reagent for CO, Schutze reagent (iodine pentoxide over silica gel) preceded by Hopcalite [manganese oxide/copper(II) oxide] oxidizes CO to CO_2 present in the carrier gas or extracted during measurement.

5.7 Absorption media for CO_2, sodium hydroxide over clay or equivalent will then absorb the CO_2.

5.8 Flux reagents for reference material. Tin, copper, or nickel granules are used as flux to accelerate the melting of reference material.

6 Apparatus

6.1 Hydrogen analyser. It will consist in a furnace capable to reach temperature of at least 2 200 °C, a thermal conductivity cell and gas purifying systems.

6.2 High purity graphite crucible, suitable for the appropriate sample types.

The impurity content should not exceed 2 µg/g.

6.3 Hydrogen free tin, copper, or nickel capsules.

6.4 Balance, with precision of 1 mg.

7 Sampling

7.1 Sampling procedure

7.1.1 Powders

Sampling is done with a tube shaped powder sampler having an inner diameter of more than 2,5 times of the maximum powder particle size. The sample shall be exposed to ambient conditions for not longer than 5 min because alterations of the powder sample due to moisture adsorption or desorption or oxidation have to be avoided. The sample has to be stored in tight containers. The gas volume in the container should be as low as possible. In case the analysis is not performed immediately after the sampling, the sample mass has to be controlled before and after storage period prior to the analysis. These precautions can be relaxed if the analysis process is made under controlled gas environment (glove box environment).

1) Reference materials are available for example from “National Institute of Standard and Technology (NIST)” or “LECO Corporation”. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of these products.

7.1.2 Pellet

When sampling the fuel pellets, ensure that pellets are not contaminated with H_2; use metal forceps or pincers for sampling pellets. The sample should be representative for the manufacturing process (e.g. storage of the pellets).

7.2 Preparation

7.2.1 Powder

Powder samples can be filled into capsules (6.3) which are subsequently closed. Alternatively, the powder samples can be inserted as pressed bodies ("green pellets" prepared without additives).

NOTE A compromise solution between precision and sustainable development (wastes recycling) is to delete the use of capsules.

7.2.2 Pellet

Sintered fuel pellets can be analysed without any preparation step. If the pellets are dried before the rod filling in the rod fabrication process, the sample should be dried before analysis to be representative of manufacturing conditions.

8 Procedure

8.1 Blank test

The analyser is checked by performing blank measurements proving the integrity of the purifying units and the tightness of the equipment. Blank values exceeding the analyser detection limit require adequate measures of correction.

8.2 Calibration

8.2.1 Calibration of the analyser

Hydrogen analyser shall be calibrated before sample measurement. There are two possibilities of calibration:

— calibration with gas;

— calibration with certified standards.

The calibration will depend on the type of analyser, it can be performed by the analyser manufacturer and/or the final user. The calibration range and the number of standards will depend on the equipment, the final use, and the range of available standards.

In case of calibration with gas, a well-defined volume of the calibration gas (5.2), which is corrected on standard conditions, is inserted and analysed. This calibration is performed three times.

In the case of calibration with certified standards, they are weighed to the nearest 1 mg accuracy.

8.2.2 Check of the calibration

To check the calibration of the equipment, reference material (5.3) is weighed to the nearest 1 mg accuracy [flux reagents (5.8) can be used to help for fusion]. The released hydrogen is determined. The measured values can differ from the certified values by not more than the total uncertainty of the analysis process. If not, the calibration is repeated.

8.3 Determination

Weigh the sample to the nearest 1 mg.

The empty graphite crucible is purified in a carrier gas stream during at least 30 s by heating at a temperature above the analysis temperature.

Insert sample (sintered pellet, green pellet, encapsulated powder) into the analyser.

Purge with carrier gas during at least 30 s.

The sample is dropped into the crucible and heated up to at least 1 770 °C.

The hydrogen content is measured, during at least 60 s to extract H_2 from all the hydrogenated compounds.

9 Calculation

Calculate the hydrogen mass fractions (µg/g sample) using Formula (1):

$$w_{H_2} = \frac{m_{H_2}}{m} \quad (1)$$

where

w_{H_2} is the hydrogen mass fractions, in µg/g sample;

m_{H_2} is the mass of the hydrogen in µg, corrected of the blank;

m is the mass of the sample, in g.

If a result expressed as µg hydrogen per g U, µg hydrogen per g(U+Pu), or µg hydrogen per g(U+Gd) is required, the results are converted as follows:

$$\left[w_{H_2}\right]_M \mu g / gM = \frac{(H\ \mu g / oxide) \times 100}{\%\ M\ content\ of\ sample} \quad (2)$$

where

$\left[w_{H_2}\right]_M$ is the hydrogen mass fractions, in µg /gM;

M is U or (U+Pu) or (U+Gd).

10 Precision

The repeatability standard deviation, Sr, of the hydrogen detection system can reach s_r = 0,18ppm → RSD = 15 % relative in the following conditions:

— 10 measurements of a reference material;

— same calibration with H_2-gas during the 10 measurements; and

— reference material of about 10 g with 1,2 µg/g of H_2;

The total uncertainty, taking into account the accuracy of the reference material and the precision error of the calibration (mainly influenced by the kinetics of moisture release and of H_2O-reduction on the

